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Feasibility of integration of an electrodialytic process into soil remediation procedure for removal of copper, chromium and arsenic

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INTRODUCTION

Soils polluted with heavy metals and arsenic compounds are a challenge for contaminated soil handling procedures. Traditionally, a remediation of such material involves excavation of the contaminated soil, followed by an immobilization of metal contaminants by solidification/stabilization technology prior to disposal of the material in a permitted landfill site or on-site. However those remedial actions based on solidification/stabilization technology are no longer considered a permanent solution because the pollutants are not removed from the contaminated media resulting in a need for future monitoring of a pollutants faith on site and questionable longevity of the solidified/stabilized materials (Dermont et al., 2008).
Therefore, there is a great need for a novel treatment technology that can efficiently separate heavy metals and arsenic from the soil. Among the technologies that have been in focus recently are: 1) flotation; 2) soil washing; 3) phytoremediation and 4) electrokinetic methods. All processes are affected by soil properties and speciation of the polluting compounds and process efficiency may have to be enhanced by chemicals addition, like surfactants, which were reported to improve washing and flotation (Reynier et al., 2013; Torres et al., 2012).
Another approach could be a combination of two technologies, like presented in this paper uniting soil washing and electrodialytic remediation. Application of the electrodialytic (ED) remediation developed at the Danish Technical University has been well described in last decades, but was mostly applied as laboratory and bench scale experiments with very limited mass of treated material (Ottosen & Hansen, 1992). The ED method combines the technique of electrodialysis with the electromigration of ions in the polluted soil. During the process it is possible to separate ions from soil with help of applied electric field to electrodes isolated from soil by ion-exchange membranes. Anions, like arsenite and arsenate, are removed to compartment with anode through a anion-exchange membrane and cations, of copper and chromium, are moved into a compartment with cathode through a cation-exchange membrane. Laboratory experiments proved that the ED remediation process applied on saturated soil was very effective for the removal of copper and to a certain extent chromium (Hansen et al., 1997). However As was not removed significantly in this system. This is mainly because the soil is acidified during the remediation, and in acidified soil As will mainly be present as uncharged species (H_3AsO_3 in case of As(III) and H_3AsO_4 in case of As(V)). Such uncharged species are not transported in the applied electric field. Faster remediation was showed to take place in a stirred suspension of soil than in the water saturated soil (Jensen et al., 2007; Ottosen et al., 2012). Moreover, increasing pH to pH=3-4 significantly increased arsenic species removal reaching a removal efficiency of 60% (Sun et al., 2012). It was also shown that remediation of the fine fraction of soil was faster and more energy efficient than remediation of the whole soil. Therefore if the contamination is primarily bound to the fine fraction of the soil, which is often the case, it may well be feasible to first implement soil washing to separate the less contaminated coarse fractions from the highly contaminated sludge, and then subject the fine fraction (sludge) to ED remediation, which would then be more efficient both due to the smaller mass to be treated and due to the higher efficiency of the treatment (Jensen et al., 2006). The concept was introduced earlier (Jensen et al., 2012).
This work aims to investigate the feasibility of application of the technology duet for decontamination of one of several former wood preservation plant left polluted by Cu, Cr and As (CCA) in Denmark. CCA was originally used in the impregnation process, and hot spot concentrations of copper, chromium and arsenic (1000-2000 mg - Cu/kg of soil, 300-600 mg Cr/kg and 200-1200 mg As/kg) are clearly above the Danish clean soil criteria of 500 mg Cu/kg, 500 mg Cr/kg and 20 mg As/kg. The Collstrop site only poses minimal risk to the nearby recipients and the groundwater resource in the area, but it is a standard site for wood preservation. The site is therefore used by The Capital Region of Denmark for testing remediation methods. The objective is that these methods in the future can be applied on similar sites where remediation is required due to risks towards groundwater and recipients.

METHODOLOGY

Soil sampling

Soil samples were obtained from two locations at the Collstrop contaminated site in Hillerød, Denmark. The samples differed in contamination level . Soil samples from location A were mainly used for lab scale investigations, and soil fines were obtained by wet-sieving the original soil through a 63µm sieve with water and soil from location B was excavated and washed in a soil washing facility Umweltschutz Ost GmbH in Germany. The initial concentrations are shown in Table 1. The soil samples were air dried at room temperature prior laboratory experiments, while for pilot investigations it was used as obtained from the soil washing facility.

Table 1 Heavy metals and arsenic content in Soil samples from the two different locations

	Location A – for lab scale investigations		Location B – excavated and washed in Germany	
	Soil-A	Fine-A	Soil-B	Fine-B
Cu	1130 ±90	8500 ±1600	183 ± 80	182 ±14
Cr	300 ±20	1900 ± 200	10 ± 5	104 ±14
As	214 ±5	2080 ± 400	220 ± 80	470 ±120

Analytical procedures

Solid samples of 1.0 g of dry soil and 20.0 mL (1:1) HNO3 were heated at200 kPa (120 ◦C) for 30 min according to Danish Standard 259. The liquid was separated from the solid particles by vacuum through a 0.45 µm filter and diluted to 100 mL. The concentrations of metals and As in prepared liquid samples were measured with ICP (Varian 720-ES, software version: 1.1.0). Examination of the pH-dependence of metals and arsenic mobilization from soil used the following procedure: 5.0 g of dry soil and 25 mL of acid, HNO_3 in various concentrations, or basic, NaOH in various concentrations, solutions were used to make soil suspensions that were mixed for 7 days to reach equilibrium. After this time the suspensions were filtered (0.45 µm) and the filtrates were analyzed.

Electrodialytic remediation – lab and pilot scale

The electrodialytic experiments in lab scale were conducted in cylindrical cells made from polymethyl methacrylate and were built from 3 compartments; two compartments with electrolytes on sides separated by ion exchange membranes from the middle compartment, where the soil slurry was placed as shown on Figure 1. An anion exchange membrane (50 cm^2, AR204 SZRA MK III from Ionics, GE Water & Process Technologies) was placed between anode (+) and middle compartment and cation exchange membrane (50 cm^2, CR67 MK III from Ionics, GE Water & Process Technologies) was placed between catode and middle compartment. Platinated rods from Permascand were used as electrodes. Electrolytes (500 mL of 0.1 M NaNO3, pH= 2 ± 0.2 adjusted with HNO3) were circulated through the electrode compartments and the soil slurry in the middle compartment remain suspended. Application of a DC electric field to electrodes immersed in the electrolytes (compartment I and III) or directly in the treated slurry (compartment II) induces water splitting reactions that depends on polarity of electrode:

- reaction on anode (+): 2 H2O → O2(g) + $4H^+$ + $4e^-$
- reaction on cathode (-): 2H2O + 2e- → H_2(g)+ $2OH^-$

A placing of electrode in the slurries compartment enabled to apply current between the slurry and one electrolyte at a time, depending what kind of ions were aimed to remove. To remove cations compartments II and III were connected, where the electrode M was working as anode and the compartment I was inert in the process. Similarly connection of compartment I and II, where the electrode M was working as catode was used to remove anions from the slurry.

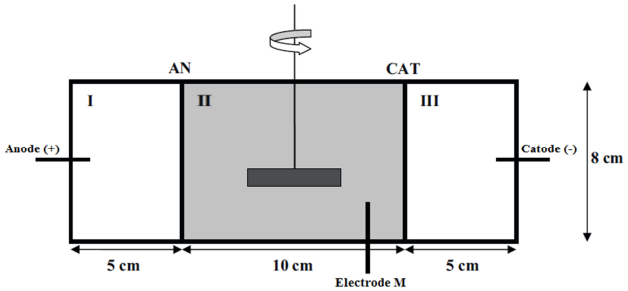

Figure 1 Principle of electrodialytic remediation of suspended soil slurry (AN – anion exchange membrane, CAT – cation exchange membrane) (Sun et al., 2012)

The experiments were performed on 35 ± 0.2 g of soil material that was suspended in 350 ± 5 mL of water, resulting in liquid to solid (L/S) ratio 10. A current of 20 ± 0.1 mA was used resulting in a current density of 0.4 mA/cm^2. After end of the experiments removal efficiency for each element was calculated as the mass of the actual heavy metal and arsenic in the electrode components (membranes, solutions in electrode compartments and on electrodes) divided by the total mass of the element found in all parts of the cell. Therefore the final results were divided into 4 groups that are defined as following:

- Anode Comp. (+) – sum of the element masses from electrolyte, anode and anion exchange membrane;
- Catode Comp. (-) – sum of the element masses from electrolyte, catode and cation exchange membrane;
- Mobilized from soil – mass of the element found in filtrate after passing 0.45 µm filter;
- Left in soil – mass of the element in dried soil after filtration with 0.45 µm filter.

The upscaled electrodialytic remediation was following the same principles as the laboratory cell, but enabled to treat 1000L of soil slurry. The compartments with ion exchange membranes where submerged in the slurry that were mixed with help of compressed air applied from the bottom of the tank, as shown on Figure 2. The upscaled plant used bigger membrane area, i.e. 2200 cm^2 each, and 25L of electrolytes were circulated. There were used different initial volumes of slurry, but the L/S ratio was the same as in the lab experiments.

The energy consumption of the ED process can be calculated by equation $E_x = \int VIdt/W$, where E is the power consumption per miligram of removed element (Wh/mg$_{removed\ x}$); V - voltage between working electrodes (V); I - current (A); t - time (h); W - the mass of the element found in the electrolytes compartment (mg). For the upscaled treatment plant power meters (SparOmeter – kWh meter from Elma Instruments) were used to measure a factual energy consumption of all electrical equipment, also for electrolytes pumps and stirring systems.

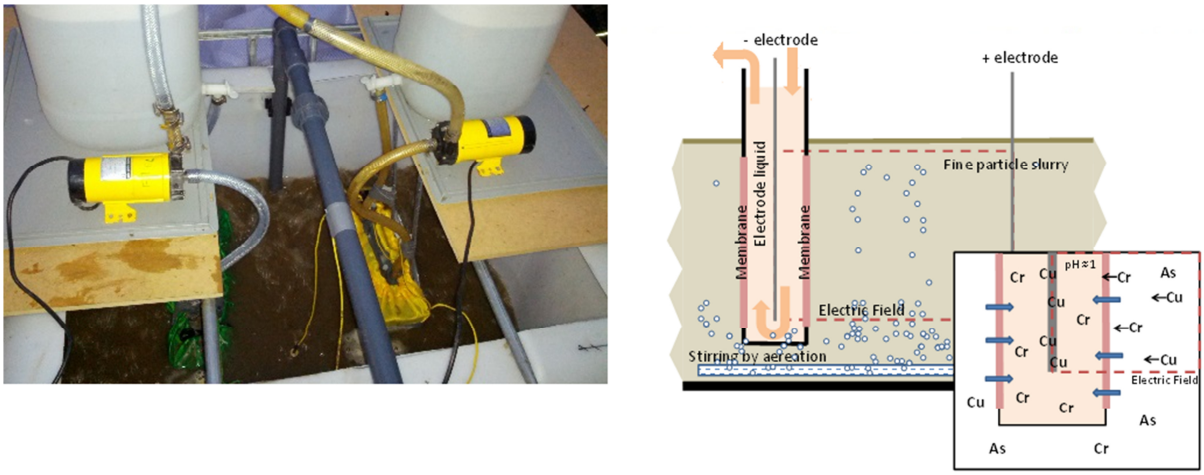

Figure 2 Left: The prototype bench scale electrodialytic treatment with aeration system (in a bottom), electrode cassettes and an electrode liquid recycling system (green with cation exchange membranes and catholyte and yellow with anion-exchange membranes and anolyte). Right: Conceptual model of electrochemical batch. Only the setup for removal of cations, Cr and Cu, is shown. For removal of As, the electrodes and membrane are reversed.

RESULTS

Soil characteristic

The particle size distribution obtained by wet-sieving of soil A indicates that the soil consisted mostly of size fraction between <1-0.125 mm (Figure 3). However these fractions are the least contaminated by As, Cr and Cu. The highest contents of Cu, exceeding the Danish clean soil criteria of 500 mg/kg, were in sand (> 1mm) and finest fractions (<0.063 mm). All fractions surpass As the criteria that is 20 mg/kg, but the highest As content was found in the finest fractions. Chromium exceeding the clean soil criteria was found only in the finest fraction. The presence of the contaminants in coarse fractions can be a consequence of organic material occurrence, especially preserved wood particles. Though accumulation of contaminants in the finest fraction of soil brings two advantages, enable to reduce mass of treated material and increase initial contaminants content. Therefore, the washing of soil B performed on 14 tonnes of material was aiming to obtain the finest fraction that would have been used in the pilot scale investigations. The outcome of soil washing was production of 4.4 tonnes of fine fraction (Fine-B), which properties can be found in Table 1. The fine-B material was only exceeding the clean soil criteria for arsenic content, as the soil-B did not have high Cr and Cu concentration when compared to soil-A.

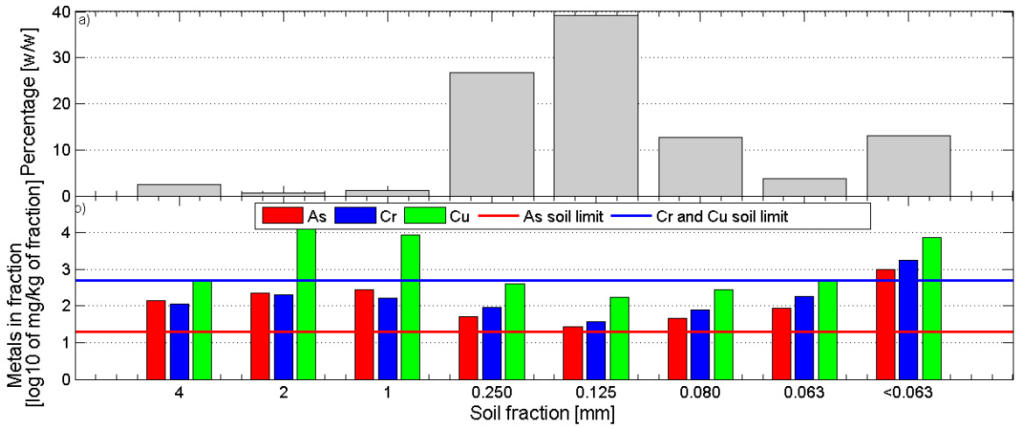

Figure 3 Particle size distribution (a) and concentration of contaminants in each fraction size for soil sample A (As, Cr and Cu soil limits refer to Danish clean soil criteria)

The pH of slurry is a crucial parameter for electrodialytic remediation as it affects heavy metals and arsenic release. The mobilization dependence on pH is presented on Figure 4. To achieve all contaminants, i.e. As, Cr and Cu, mobilization the pH shall be decreased to below 2, where about 90% of Cu is dissolved. For mobilization of As and Cr the pH even has to be decreased to pH<1 to achieve more than 80% of mobilization. The mobilization of those compounds at low pH may be due to dissolution of contaminant bearing minerals and aluminum and iron hydroxides that are known for their adsorption capacities (co-precipitation). However the low pH conditions are limiting occurrence of arsenic anions, as its species starts to dissociate at pH above 2 (pK_{a1} of arsenate-H_3AsO_4 is 2.2 and pK_{a1} of arsenite-H_3AsO_3 is 9.3). Applying the basic conditions, especially pH above 12, reveals a different pattern for contaminants mobilization. At high pH the arsenic distinguish oneself as the most mobilized. The phenomena may be explained with desorption of As anions from amorphous iron oxide that starts at pH above 9 (Dixit and Hering, 2003).

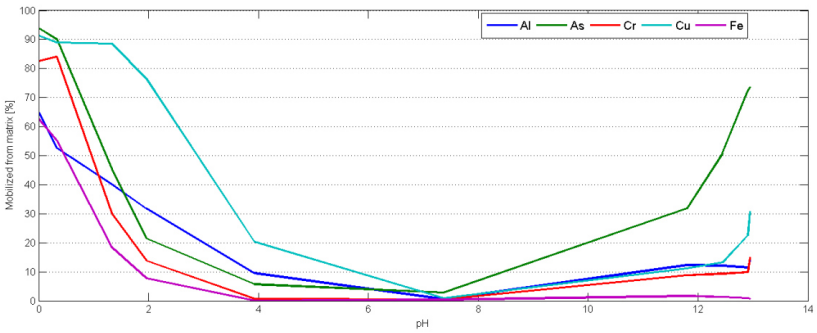

Figure 4 Dependency of pH on metals and As mobilization from soil-A

ED- pilot and laboratory results

The evolution of main parameters in pilot electrodialytic treatment of soil-A suspension is presented on Figure 5. From a beginning of the treatment no significant Cu and As removal to the electrolytes was observed. After adding nitric acid to the soil suspension an increase in concentration of the contaminants in electrolytes could have been detected (Fig 5d). Addition of acid to the soil slurry decreased pH and resulted in metals and arsenic release to water phase enabling their removal through ion exchange membrane driven by applied current. Also addition of acid increased suspensions conductivity and as a consequence decreased voltage required to maintain applied current that results in a lower energy consumption of power supply connected to electrodes. Even though the lower arsenic mobilization occurs at higher pH this condition would be preferable to apply in electrodialytic process due to arsenic dissociation and its occurrence in anionic form. Therefore the best results for soil decontamination were obtained in laboratory experiments, when a first phase aimed to remove cations at low pH and second phase aimed to remove anions at high pH. For example a lab ED experiment on fine-A material, where during first 2days aimed to remove cations reaching pH 1.5 and 2nd phase, lasting 8 days, where anions were removed at pH 10-11 enabled to achieve 70% of Cu removal and 45% of As removal efficiency. And application of the ED lab treatment on the fine-B material, where only anions were removed at high pH enabled to remove above 70% of arsenic, which is a better results achieved in other studies, when soil fines suspension

was treated in acidic conditions (Sun et al., 2012). However the soil fines quality and process conditions shall not be neglected, as they influence the ED treatment.

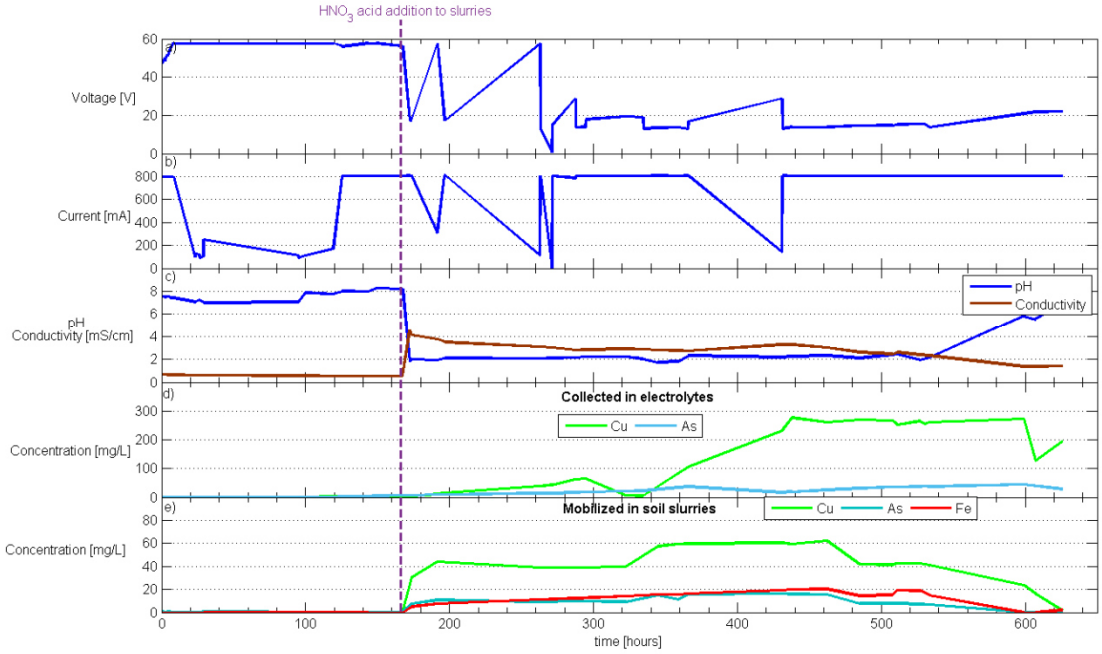

Figure 5 Variations of main parameters during ED pilot remediation applied for soil-A suspension (45kg of soil in 515 L of water): applied voltage (a) and current (b) to electric field; pH and conductivity of suspension (c); concentration of Cu and As in electrolytes (d) and Cu, As and Fe mobilized to water phase (e)

The treatment of the fine-B material in pilot plant focused only on As removal, as only this element was exceeding the criteria. Therefore the process has been performed only at high pH conditions that can be reached in two different ways: by producing hydroxide anions with help of reaction on a cathode submerged in soil slurry or by dosing hydroxide to the slurry. Addition of NaOH increased pH immediately from 7.5 to 10.8 and resulted in some arsenic mobilization. Production of sufficient amount of ^{-}OH on catode requires time and energy before making arsenic species available to removal. In other hand addition of other anions, especially when dosing NaOH, may have a consequence in long-term process efficiency as hydroxide and arsenic anions will compete to pass through anion exchange membrane. Comparison of processes efficiency, with regards to energy used for removal of As ($Wh/mg_{removed\ As}$) is presented on Figure 6. Three different pilot treatments are compared with the ED laboratory experiment on fine-material. The laboratory experiment was the most efficient with regards of energy used for ED, i.e. energy of power supply to apply current between the electrodes, which can be explained by the small size of the laboratory cell and amount of material used. The pilot treatment required 20-100 fold higher energy to remove arsenic from slurry, which indicates that electric current was not as efficiently distributed in the slurry container as it was in the laboratory cell. However the differences in power used for maintaining suspension reveals that in the laboratory experiment a low cost of energy used for ED is only a minor part of total energy spent on the treatment, as a major part of the energy was consumed by a stirring system. On the contrary the pilot setups with the fine-B material have used a very low energy for stirring, as it was applied only twice a week for period of 15 minutes, which seemed to be sufficient to keep a material in suspension to some degree. More energy was used in case of treatment of soil-A suspension, as the slurry were constantly mixed, but it has not been enough to keep a coarse fraction of soil suspended. However the energy used for ED itself is much alike for treatment acidified slurry of soil-A and basic slurry of fine-B, which can be explained by immediate arsenic mobilization and its availability for removal. As for pilot treatment of fine-B without initial pH change the process started at pH 7.5, where less As is mobilized, resulting in much lower energy efficiency for its removal. The processes are continued to reveal mechanisms of As removal and built a ground for process optimization.

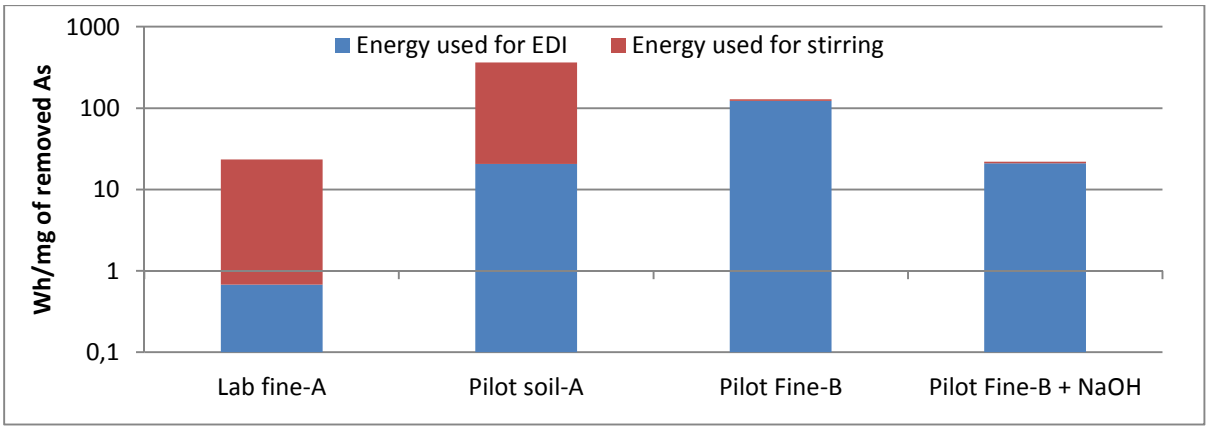

Figure 6 Comparison of energy of the ED processes used for removal of As from soil material suspensions in laboratory cell („Lab fine-A") and in pilot runs with soil A („Pilot soil-A" - refers to energy used since suspension acidification) and fine B with NaOH addition („Pilot Fine-B+NaOH") and without any chemicals addition to the suspension („Pilot Fine-B")

Conclusions

Laboratory studies proved that it is possible to apply electrodialytic remediation for separation of arsenic, chromium and copper from soil materials. The amount of treated material can be reduced with help of soil washing that enables to separate the most contaminated soil fraction, which was found to the finest fraction. However different approaches have to be applied to remove cations and anions, especially when scaling up the process. To remove cations it is necessary to mobilize them at low pH, bot for anions removal, especially arsenic high pH of the suspension has to be used to have sufficient arsenic mobilization and anions forms. The ED remediation was found to be feasible for up-scaling. The factors influencing the ED pilot scale, beside pH of treated suspension, is the stirring routine to maintain material suspension. The pilot plant investigations are ongoing and aim in defining the process parameters that shall be improved by proper equipment and process design.

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